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APPLICATION OF US-EPA METHOD 29:

Sampling of Metals Emissions from Stationary Source

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Abstract

This report summaries the results of sampling (and analyses) of stack flue gas of P.T. Semen Cibinong's Kiln, located at Jl. Raya Narogong, Desa Nambo, Cileungsi, Bogor. The test was aimed to determine concentrations of emitted metals (As, Cd, Cr, Pb, Hg and Tl) concentrations. The conditions of the kiln tested were maintained at its normal operation. The metals were sampled from the flue gas at 3 (three) replicates. The metals concentrations in all three tests were well below the standard as stipulated in Kep-06/BAPEDAL/02/1999. This stack sampling work was carried out with the strict procedures specified by United States Environmental Protection Agency (US-EPA), Method No. 29. The laboratory analysis of metals were conducted by Analitika Sejahtera Lingkungan (ASL) laboratory, Bogor. The procedures of both stack sampling and laboratory analyses have followed a quality assurance/ quality control (QA/QC) program as an integral part of the overall technical effort.

Keywords: *US-EPA Method 29, metals, traverse points, isokinetic sampling, linear velocity*

1. INTRODUCTION

1.1 Background

Cement kiln is known as a waste destruction reactor since it uses relatively high temperature during the process. It can almost spontaneously destruct all the wastes including heavy metals.

In cement kiln, there are several types of kilns, namely long wet, long dry, pre-heater dry, pre-heater/pre-calciner dry, etc. For the most part, Ministry of Environment of Indonesia regulates these different types on the same basis. There is a general concept, which states that the amount of toxic compounds emitted from a combustion source depends on the concentration of toxic compounds in the fuel and the combustions conditions. While this concept is acceptable on a broad basis, when applying it to cement kiln, it also must properly take into account specific characteristics of cement kilns, which differentiate this process from other combustion devices. Because of the much larger thermal mass and the much greater time, temperature, and turbulence associated with a cement kiln process it is unlike any other combustion devices.

In order to know how much metals concentrations emitted from the kiln it is useful to measure them from the kiln stack. This study is, therefore to carry out the stack sampling work using established standard method. Since there has not been such a standard available in Indonesia, the sampling used was a US-EPA Method 29.

1.2 Aim of the Study

The aim of the study was to carry out metals stack measurements from cement kiln, using US-EPA Standard Method 29. The targeted metals were arsenic (As),

cadmium (Cd), chrome (Cr), lead (Pb), mercury (Hg), and thallium (Tl).

2. SCOPE OF WORK

2.1 Sampling Site Description

PT. Semen Cibinong (now Holcim) produces portland cement using pulverized coal as the kiln's primary fuel source. A description of facility of the kiln at which the test was conducted is presented below.

2.1.1 Description of Kiln

Raw mill products which are stored in the two-18 meter diameter blending silos are fed automatically into pre-heater through bucket elevators and pump systems.

The pyro-processing system consists of a four-stage re-circulating feed calcining (RFC) system with a three-support rotary kiln and a reciprocating grate cooler. The system is capable of producing 4600 Tons per day of clinker. Exhaust gas from one-stage pre-heater is sucked by pre-heater fan. It is utilized as heat in the raw mill and the coal mill or could be directly passed through the ESP after its temperature is reduced in the conditioning tower. The hot clinker (approx. 1450^{o}C) exits the kiln and is cooled in a reciprocating grate cooler. Air is forced by fans into the cooler to cool the clinker. Secondary air is passed in drop box and re-circulated into calciner for combustion via swirl chamber of pre-heater. Some of cooler exhaust gas is used to heat cyclone and then sucked by tertiary fan and sent to the conditioning tower. Finally, clinker product is kept in clinker silo with addition of gypsum in the finished mill to produce cement.

It is used an indirect firing system by coal mill. This mill is designed to grind and dry up to 30 Tons/hour of wet coal at 20 micrometer screen. The heat source is from air heater or kiln/ pre-heater exhaust gas and re-circulates exhaust heat. Before entering into stack, exhaust gas is cleaned from the fine coal in the plenum pulse dust collector. This fine dust coal is then collected in a 100 tons capacity of bin before it is used as a fuel in main kiln and calciner burners. The transporting device of the pulverized coal to the burner uses pump system.

2.1.2 Air Pollution Control Equipment

The air pollution control systems (APCs) for the kiln is a three-stage electrostatic precipitator (ESP). Combustion gases from the pre-heater/kiln enter the ESP via conditioning tower. Evaporated moisture is used to condition the combustion gases. The gas conditioning function is taken over by the conditioning tower water spray. The cleaned combustion gases enter an induced fan that exhausts to a stack.

After exiting the kiln, combustion gases enter into the suspension pre-heater and then enter the ESP. The ESP consists of one chamber with three fields. The ESP is designed to treat around 1,030,000 m^3/ hour at a temperature of about 116^{o}C (maximum temperature of 300^{o}C) and at an efficiency of 99.9 %.

ESP dimension is 16.94 meter chamber width, a 14 meter field height, and 3x4.5 meter field length. Total collecting area of the ESP is 14,742 m^2, pressure drop over the ESP is 2.5 mm water gauge, number of chamber is one and number of fields per chamber are 3 (three) units.

2.1.3 Description of Exhaust System and Sampling Location

The emitted gases are exhausted through a 60 meter high stack having a 4.5 meter inside diameter. Figure 1 shows the sampling port and the traverse point configurations in the stack.

For aiding in the representative measurement of metals emissions from a stationary source, a measurement site where the effluent stream is flowing in known direction is selected. Then, the cross-

section of the stack is divided into a number of equal areas. After that, a traverse point is located within each of these equal areas (see Table 1).

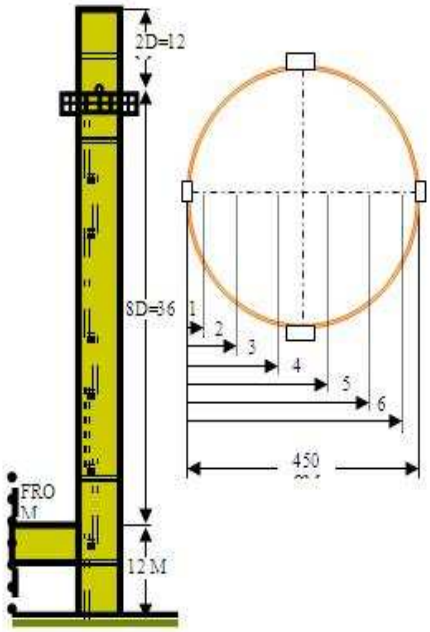

Figure 1. Stack, sampling ports, and traverse point configurations

2.2 Sampling and Analytical Procedures

Sampling of heavy metals from gas stream requires a technique known as "isokinetic sampling". Sampling is isokinetic when the inlet of the sampler is aligned parallel to the gas streamlines and the gas velocity entering the probe is identical to the free stream velocity approaching the inlet (see Figure 2).

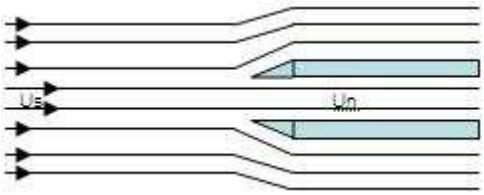

Figure 2. Isokinetic sampling, when gas linear velocity of stack equals to that of nosel (u_s=u_n).

Table 1. Traverse points distance from the inside wal

Traverse Point	Distance from the inside stack wall (cm)
1 and 7	19.8
2 and 8	66.7
3 and 9	133.2
4 and 10	316.8
5 and 11	384.3
6 and 12	430.2

If it is isokinetic sampling, there is no particle loss at the inlet regardless of particle size or inertia. A failure to sample isokinetically may result in a distortion of the size distribution and a mis-representation of the concentration. Figures 3 and 4 show graphically typical non-isokinetic sampling. Those are when the linear velocity through a sampling nozel (u_o) is higher or lower than that of stack (u_s).

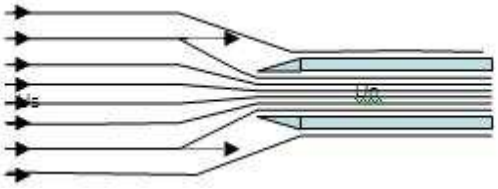

Figure 3. Non-isokinetic sampling, when gas linear velocity of stack lower than that of nozel (u_s < u_n).

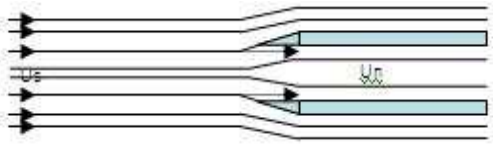

Figure 4. Non-isokinetic sampling, when gas velocity of stack greater than that of nozel (u_s > u_n).

To do isokinetic sampling requires some data for setting up the sampling rate. Therefore before isokinetic sampling is performed, these prerequisite data must be determined from the stack using standard methods as outlined by Kep. Ka. BAPEDAL

No. 105/1996.These methods are for the determination of sampling site and traverse points, stack gas velocity and volumetric rate, molecular weight, and gas moisture content. The general procedure to complete the isokinetic stack sampling is outlined in Figure 5.

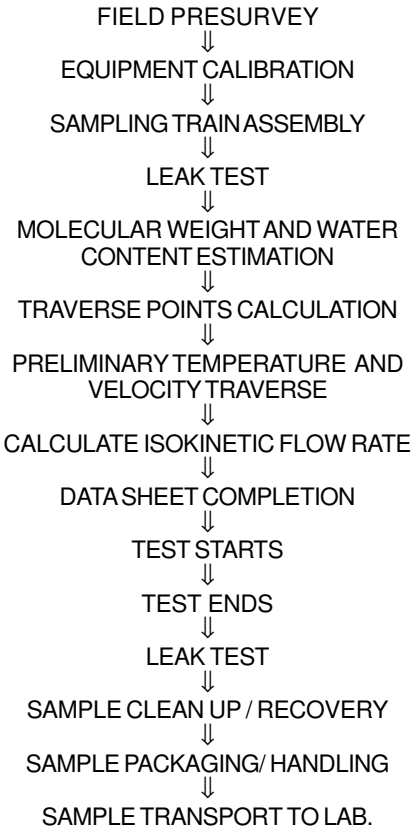

Figure 5. Outline of isokinetic stack sampling procedures.

2.1.1 Metals Measurement

Metals sampling method was not available in the BAPEDAL-Indonesia protocol and therefore it used US-EPA Method 29. This method is applicable to sample particulate and some targeted heavy metals of arsenic (As), Thallium (Tl), cadmium (Cd), chromium (Cr), lead (Pb) and mercury (Hg). The use of a special glass-lined sampling probe for this test was necessary to avoid contamination.

Metals from the emitted gas stream were pulled into the probe isokinetically. The solid samples were collected in the probe and on a heated glass fiber filter maintained at a temperature of about 120°C. The gaseous emissions were then collected in an aqueous acidic solution of hydrogen peroxide (analyzed for all metals including Hg) and an aqueous acidic solution of potassium permanganate (analyzed only for Hg). The total particulate collected on the filter and probe were determined gravimetrically in the laboratory and

Table 2. Data of velocity measurement and the calculated flow rates.

Run #	Velocity m/s	Flow rate @ACT-m3/h	Flow rate @STDm3, dry basis
1	18.36	1,050,483	851,790
2	16.83	963,364	777,224
3	17.6	929,777	730,564
4	17.7	1,013,074	812,164
5	17.45	998,403	796,195
6	17.7	1,012,877	804,778
7	18.6	1,065,750	837,143
8	18.65	1,067,480	789,879
9	18.63	1,065,961	813,774
Mean	17.95	1,018,574	801,501
SD	0.55	38,973	24,921

Note:
ACT : Actual condition
STD : Standard condition
SD : Standard Deviation

the mass of each targeted metal collected on the filter and impingers was analyzed using an appropriate Atomic Absorption Analyzer.

The sampling train selected to collect the particulate and metals was a Graseby Andersen UP-EPA Method 5 train modified for total particulate and metals (As, Tl, Cd, Cr, Pb, and Hg). The train arrangement is shown in Figure 6, which used a series of six impingers.

Samples for both metals and particulate were taken isokinetically, and conducted in the same sampling time. However, two different absorbents were used

for metals sampling, i.e. acidic solution of hydrogen peroxide for all metals including Hg and acidic solution of potassium permanganate only for Hg.

These impingers contain the following reagent:

- 100 ml 5% HNO_3 in 10% H_2O_2
- 100 ml 5% HNO_3 in 10% H_2O_2
- 100 ml 4% $KMnO_4$ in 10% H_2SO_4
- 100 ml 4% $KMnO_4$ in 10% H_2SO_4
- 100 ml distilled H_2O
- 200 g silica gel.

3. DATA/RESULTS

3.1 Gas Flow Rate Data

The gas flow rate is calculated from linear gas velocity measured with S-type pitot tube times cross sectional area of the stack. During the test, nine velocity measurements were made. These velocity data are presented in Table 2.

3.1 Metal/ Particulate Data

Metal and particulate sampling was done using Method 29 US-EPA. There were 7 (seven) recovered bottling samples to be analyzed in the laboratory for both particulate and targeted metals content. Six different heavy metals were analyzed using Atomic Absorption Spectrometry method. Using stack sampling data and the laboratory analyses for each recovered sample, their concentrations could be calculated as presented in Table 3.

3.2 Gas Flow Rate

The average velocity measured using S-type pitot tube was about 17.95 meter per second. With a 4.5 meter stack diameter it resulted about 1,018,574 actual m^3 per hour flow rate at average temperature of 100 ^oC. This value closes to the designed value of 1,030,000 actual m^3 per hour at temperature of 158^oC. The flow rates varied with a deviation standard of 38,973 m^3 per hour or about 3.8% of the mean value.

3.3 Metals Concentrations

Metals stack sampling tests were carried out at 3 (three runs while burning hazardoys waste fuel (HWF) containing sodium bichromate solution and lead stearate powder. The rate of HWF consumption during the test were 2.5, 2.1,

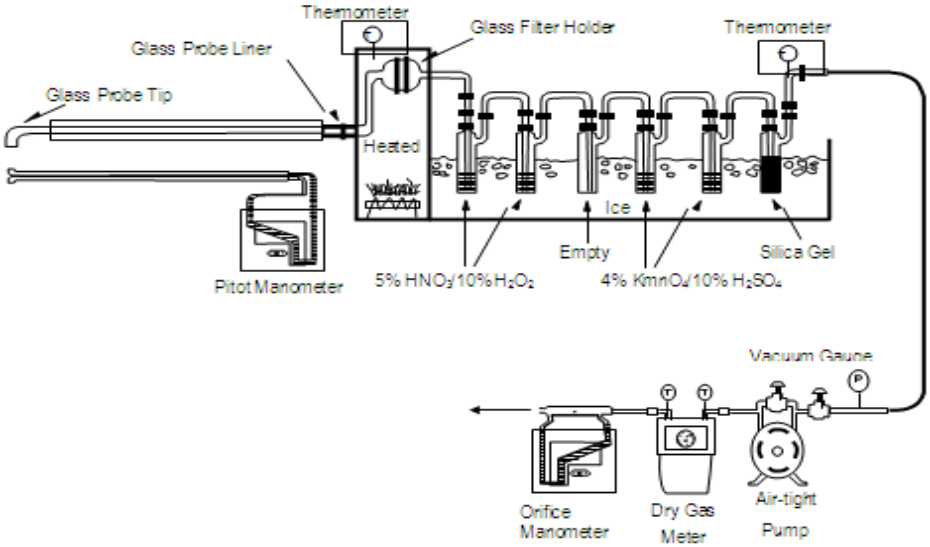

Figure 6. Metals sampling train (Method 29 - USEPA)

and 2.1 Tons per hour combined with 11.0, 11.3 and 11.3 Tons of coal per hour for tests 1, 2 and 3, respectively. The spiked materials contained in the HWF was analyzed and the values are 749 and 513 mg/kg wet weight for Cr and Pb, respectively. The concentrations of Hg and Tl were 2.22 and 40 mg/kg wet weight even though without spiking.

Isokinetic calculations of metals stack sampling test were found to be about 96, 95 and 96 % for the respective tests 1, 2 and 3. All test runs meet the Code acceptability requirements for isokinetic values ranging from 90 to 110 %.

The metal concentrations of As, Cd, Cr, Pb, Hg, and Tl, even corrected at 7% O_2 as shown in Table 3, were all well below the existing standard as stipulated in KEP-03/ BAPEDAL/09/95, i.e. 1.0, 0.2, 1.0, 5.0, 0.2 and 0.2 mg/STD m^3 @ 10% O_2, respectively. Table 3 also shows the results of calculated emission rates of metal components. By averaging the results from tests # 1 and 3, it was found that the respective emission rates of As, Cr, Pb, and Hg were 0.00025, 0.0035, 0.0035 and 0.018 kg/h STD condition, dry basis and @ actual O_2 content. The emission rates of Cd and Tl were found to be below detection limit (bdl).

The test # 2 was for representing the worst case scenario of ESP operation. It indicated however that the worst operation of ESP performance did not affect high emission in metals.

4 DISCUSSION

4.1 Gas Flow Rate

The average velocity measured using S-type pitot tube was about 17.95 meter per second. With a 4.5 meter stack diameter it resulted about 1,018,574 actual m^3 per hour flow rate at average temperature of 100 ^oC. This value closes to the designed value of 1,030,000 actual m^3 per hour at temperature of 158^oC. The flow rates varied with a deviation standard of 38,973 m^3 per hour or about 3.8% of the mean value.

4.2 Metals Concentrations

Metals stack sampling tests were carried out at 3 (three runs while burning hazardoys waste fuel (HWF) containing sodium bichromate solution and lead stearate powder. The rate of HWF consumption during the test were 2.5, 2.1, and 2.1 Tons per hour combined with 11.0, 11.3 and 11.3 Tons of coal per hour for tests 1, 2 and 3, respectively. The spiked materials contained in the HWF was analyzed and the values are 749 and 513 mg/kg wet weight for Cr and Pb, respectively. The concentrations of Hg and Tl were 2.22 and 40 mg/kg wet weight even though without spiking.

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Table 3. Summary of metals and particulate stack sampling data, concentrations, and emission rates.

Data recorded/ Calculated	Test 1	Test 2	Test 3
- Sampling time, min.	120	120	120
- Gas volume, STD m^3.	2.808	2.656	2.806
- Stack Temp., ^oK.	371.1	394.1	383.3
- Linier gas vel., m/s.	18.6	18.65	18.63
- Flowrate, @ACTm^3/h	1,065,750	1,067,480	1,065.96
- Flowrate, @STDm^3/h,dry basis	837,143	789,879	813,774
- Isokinetic value, %	95.66	94.59	95.52
- Actual O_2 content	15.1	15	15.2
Concentration @ ACT. O_2 content, STD-dry basis			
- As, mg/m^3	0.00066	0.000974	0.000463
- Cd, mg/m^3	bdl	0.000044	bdl
- Cr, mg/m^3	0.00445	0.004191	0.003336
- Pb, mg/m^3	0.005	0.005034	0.003804
- Hg, mg/m^3	0.022	0.023266	0.022024
- Tl, mg/m^3	bdl	bdl	bdl
Concentration @ 7% O_2 content, STD-dry basis			
- As, mg/m^3	0.0016	0.0023	0.00113
- Cd, mg/m^3	bdl	0.0001	bdl
- Cr, mg/m^3	0.01065	0.00987	0.00813
- Pb, mg/m^3	0.01197	0.01186	0.00928
- Hg, mg/m^3	0.05274	0.05481	0.05371
- Tl, mg/m^3	bdl	bdl	bdl
Emission rate @ACT. O_2 content, STD-dry basis			
- As kg/h	0.001	0.0008	0.0004
- Cd, kg/h	bdl	bdl	bdl
- Cr, kg/h	0.004	0.0033	0.0027
- Pb, kg/h	0.004	0.004	0.0031
- Hg, kg/h	0.018	0.0184	0.0179
- Tl, kg/h	bdl	bdl	bdl

Note: bdl : below detection limit

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